Synthesis and Photoluminescence of CaAlBO4:RE3+(RE=Dy & Eu) Phosphor

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Abstract: A series of doped CaAlBO4:RE3+ (RE = Dy and Eu) compositions were synthesized by wet chemical method and their photoluminescent (PL) properties were systematically investigated to ascertain their suitability for application in light emitting phosphor in lamp industry. The X-ray diffraction (XRD) pattern and surface morphology data indicates that Dy3+ and Eu3+ ions are successfully occupied non centrosymmetic site in orthorhombic crystalline phase of CaAlBO4. The microstructures of CaAlBO4 are studied by scanning electron microscope (SEM). The PL emission spectra of CaAlBO4 Eu suggests the presence of both Eu3+ as well as Eu2+ ions. The PL emission spectra of Eu3+ ion was observed at 592 nm and 614 nm in red region while Eu2+ was observed at 430 nm in blue region in CaAlBO4Eu under 393 nm excitation. Emission at 592 nm and 614 nm are assigned to 5D0 → 7F2 transition in the blue region in the same phosphor. Moreover, PL emission spectra of CaAlBO4: Dy was observed at 577 nm in yellow region and at 483 nm in blue region on the excitation of 351 nm. It is well known that the blue (484 nm) emission band corresponding to the 4F9/2 → 4H15/2 magnetic dipole transition and the yellow (577 nm) emission corresponding to the 4F9/2 → 4H13/2 electric dipole transition. At the higher dopant concentration emission intensity quenched due to the decreased critical distance (Rc ≈ 35.81 Å) between Dy3+ ions similarly critical distance between Eu3+ ions was Rc ≈ 48.60 Å for maximum dopant concentration 0.2 mol.%. A series of doped CaAlBO4:RE3+ (RE = Dy and Eu) compositions were synthesized by wet chemical method and their photoluminescent (PL) properties were systematically investigated to ascertain their suitability for application in light emitting phosphor in lamp industry. The X-ray diffraction (XRD) pattern and surface morphology data indicates that Dy3+ and Eu3+ ions are successfully occupied non centrosymmetic site in orthorhombic crystalline phase of CaAlBO4. The microstructures of CaAlBO4 are studied by scanning electron microscope (SEM). The PL emission spectra of CaAlBO4 Eu suggests the presence of both Eu3+ as well as Eu2+ ions. The PL emission spectra of Eu3+ ion was observed at 592 nm and 614 nm in red region while Eu2+ was observed at 430 nm in blue region in CaAlBO4Eu under 393 nm excitation. Emission at 592 nm and 614 nm are assigned to 5D0 → 7F2 transition in the blue region in the same phosphor. Moreover, PL emission spectra of CaAlBO4: Dy was observed at 577 nm in yellow region and at 483 nm in blue region on the excitation of 351 nm. It is well known that the blue (484 nm) emission band corresponding to the 4F9/2 → 4H15/2 magnetic dipole transition and the yellow (577 nm) emission corresponding to the 4F9/2 → 4H13/2 electric dipole transition. At the higher dopant concentration emission intensity quenched due to the decreased critical distance (Rc ≈ 35.81 Å) between Dy3+ ions similarly critical distance between Eu3+ ions was Rc ≈ 48.60 Å for maximum dopant concentration 0.2 mol.%

Keywords: CaAlBO4; Wet chemical method; Concentration quenching; XRD; SEM and PL.

1. Introduction

Borate compounds are well known remarkably for their use in industries and mineralogy. Metal borates have excellent mechanical properties, good chemical inertness and high stability under high temperature, light weight, and low thermal expansion coefficients. Calcium borate is a potential material for applications in ultraviolet (UV) light sources, light emission diodes (LEDs), and luminescent phosphors, ceramic coatings, glass fibres and dielectric devices. Calcium borate glasses are potential candidates for optical applications due to their ease of shaping as large bulk samples or fibers [1]. Since their discovery, the uses of lanthanides in phosphors have found numerous applications in, for example, Scintillators, luminescence immunoassay and X-ray detector systems. One of the earliest applications was their use in phosphors for domestic lamps. The lanthanides possess unique properties which are responsible for their wide range of applications.

Eu2+-doped phosphors usually show intense broad-band emission from deep blue to red region of electromagnetic spectrum. The emission occurs due to electronic transition between 4f7 ground state and 4f6 5d1 excited state [2,3]. Since the 5d orbital is exposed to the surrounding ions the radiative transitions highly influenced by the crystal field components. Consequently, the wavelength of maximum emission strongly depends on the type of the host crystal [2,4].

The authors noted very sluggish crystallization behavior for the most B2O3 rich mixtures, and subsequent wetting and autoclave treatment at 600°C became necessary to obtain crystalline products. Two ternary phases were detected, CaAlBO4 and CaAl2B2O7. The structure of CaAlBO4 (Cc2, ρ = 2.60 g/cm³, a = 8.269 Å, b = 15.227 Å, c = 5.733 Å) is characterized by low coordination numbers for all cations: Ca is six-coordinate, Al shows tetrahedral coordination and boron is three-coordinated by O [5]. Two modifications were assumed for CaAl1-B2O7: α-CaAl1-B2O7 (below 830 °C, R 3c, ρ = 2.44 g/cm³, a = 8.104 Å, c = 46.33 Å) with a structure of ABC-stacked modules of CaO6 octahedra, AlO4 tetrahedraand trigonal BO3 groups [6]; β-CaAl1B2O7 is assumed to be monoclinic [7]. Here we concentrate on the preparation of CaAlBO4:RE3+ by wet chemical method. PL emission spectra of CaAlBO4: Eu phosphor under UV excitation shows prominent Eu3+ emission peak due to 5D0 → 7F2 transition in the orange/red region of the visible spectrum while Eu2+ emission peak due to 4F9/2 → 8S7/2 transition in the blue region in the same phosphor. Moreover, PL emission spectra of CaAlBO4: Dy was observed at 577 nm in yellow region and at 483 nm in blue region on the excitation of 351 nm. It is well known that the blue (484 nm) emission band corresponding to the 4F9/2 → 4H15/2 magnetic dipole transition and the yellow (577 nm) emission corresponding to the 4F9/2 → 4H13/2 electric dipole transition.

2. Experimental

CaAlBO4 phosphor was prepared by wet chemical method. In this process, Calcium nitrate Ca(NO3)2(99.9%), Aluminium nitrate Al(NO3)3(99.9%), Boric acid H3BO3(99.9%) and Ammonium nitrate NH4NO3 used as oxidizer (All of A.R.Grade) were taken as raw materials in exact stoichiometric proportion. In addition this, rare earth elements as Dy2O3 (99.9%) and Eu2O3 (99.9%) were also taken with molar concentration as dopant respectively.

All the chemicals were dissolved separately in 50ml double distilled de-ionized water to get clear transparent solutions.
Mixture of all the solutions which is nothing but the CaAlBO4: Ln solutions were then heated to 80°C for 8 hrs on magnetic stirrer. The dried sample was then crushed using mortar pestle and quenched at 200°C for 2 hrs so as to obtain a luminescent CaAlBO4 borate phosphor. This phosphor was then taken for characterization. The crystallographic phase identification of synthesized powder samples was carried out by X-ray diffraction (XRD, PHILIPS P Analytical XPert-PRO Diffractometer) using Cu-Kα wavelength ($\lambda=1.54060 \text{ Å}$) and scanning in 20 range from 10° to 80°. The emission and excitation spectra were measured on a SHIMADZU RF-5301 PC fluorescence spectrophotometer. The surface morphology of CaAlBO4: RE3+ (RE: Dy and Eu) was performed by a scanning electron microscope (SEM: JEOL-JSM-6360LV).

3. Results and Discussion

3.1 Crystal structure and surface morphology of CaAlBO4

The XRD pattern of the CaAlBO4 presented in fig.1, which is in good agreement with the XRD data of standered CaAlBO4 with JCPDS card (19-0204). This compound crystallizes in an orthorhombic unit cell of $a = 8.27 \text{ Å}$, $b = 15.23 \text{ Å}$ and $c = 5.73 \text{ Å}$. The microstructures of CaAlBO4 are studied by scanning electron microscope (SEM). The sample synthesized through wet chemical route; platelet like structures with other fluffy shapes is obtained with non-uniform distribution.

3.2 PL characteristics of CaAlBO4:Dy3+

Figure 1: X-ray diffraction pattern of CaAlBO4 host

Figure 2: Surface morphology of CaAlBO4 host

Figure 3(A): PL emission spectra of CaAlBO4 under excitation of $\lambda_{ex}=351$nm.

Figure 3(B): The variation of PL intensity with Dy3+ concentration
The emission spectra of CaAlBO$_4$:Dy$^{3+}$ phosphors recorded excited at UV (351 nm) light as shown in fig.3.(A) Excitation spectrum also shown in fig.3.(A), the prominent narrow absorbance band centered at 351 nm recorded at the emission 576 nm. There are two peaks observed from the emission spectra of the phosphor. The first two prominent peaks centered around 484 nm and other 576 nm. These emission peaks in the blue, and yellow region are the characteristics emission of the Dy$^{3+}$ ions and frequently seen in Dy$^{3+}$ doped phosphors [8-11].

The peaks position and the Y/B (yellow/blue) intensity ratio altered due to the influence crystal field effect of the host materials on the emission of Dy$^{3+}$ ions. It is well known that the blue (484 nm) emission band corresponding to the $^4$F$_{9/2} \rightarrow ^4$H$_{15/2}$ magnetic dipole transition less influenced by crystal field effect compare to the yellow (577 nm) corresponding to the $^4$F$_{9/2} \rightarrow ^4$H$_{13/2}$ electric dipole transition, their $\Delta J=2$ ultra-sensitive transition[12].It is well known that the blue emission is of magnetic dipole origin and the yellow one is predominant only when Dy$^{3+}$ are located at low-symmetry sites with no inversion centers [13]. Since emission intensity of the blue emission is stronger than that of the yellow one in the investigated phosphors, which suggests that there is very little deviation from inversion symmetry in the investigated phosphors.

In our case the Dy$^{3+}$ ion may enter the host lattice to substitute Ca$^{2+}$ or Al$^{3+}$ or it may be located on surfaces of the crystals due to the porous structure. It is clear from the photo-luminescence spectra that in the Dy$^{3+}$ doped phosphor, energy transfer from the host to the Dy$^{3+}$ activator ions occurs. The ionic radii of Dy ions is 91.2 pm, which is similar to those of the Ca$^{2+}$ ions (99 pm). In our case the Dy$^{3+}$ ion may enter the host lattice to substitute Ca$^{2+}$ or locate on surfaces of the crystals lattice. It's substitution at Ca$^{2+}$ site in CaAlBO$_4$ will lead to less distortion and induce more oxygen vacancies in the host phosphor. The charge compensating effects in the immediate vicinity is likely to influence the local site symmetry of CaAlBO$_4$ host. Dy$^{3+}$ ions should occupy statistically both cation positions (Ca$^{2+}$) in the unit cell. It would naturally cause a substantial number of vacant sites in the oxygen ion array and then expand the lattice to decrease crystal density[14], reported that the oxygen vacancies might act as the sensitizer for the energy transfer to the rare earth ion due to the strong mixing of charge transfer states result in the highly enhanced luminescence. But excess oxygen vacancies in the host would destroy the crystallinity inevitably, which leads to quenching of the luminescence [15]. As Dy$^{3+}$ ions progressively replace the Ca$^{2+}$ ions, it can enhance PL emission intensity and progressively reduce symmetry factor. The low-symmetry location of Dy$^{3+}$ results in predominant emission of $^4$F$_{9/2} \rightarrow ^4$H$_{15/2}$ transition in CaAlBO$_4$ host.

In principle, if there is an increase in concentration of the lanthanide ions in a given material it should be accompanied by an increase in the emitted light intensity, but it has been established that such behavior occurs up to a certain critical concentration [16]. Above this critical concentration the luminescence intensity starts to decrease. This process is known as concentration quenching of the luminescence.

Concentration quenching occurs as a result of a very efficient energy transfer process between the luminescent centers; it starts to have significant effect at a concentration for which there is a considerable reduction in the mean distance between the interacting centers. Two mechanisms are generally invoked to explain the concentration quenching: energy transfer between the lanthanide ions and defects of the host, and interactions between the lanthanide ions.

In the first case due to a very efficient energy transfer, excitation energy migrates to a large number of centers being finally transferred to lattice defects or impurity ions that act as energy acceptors. These acceptors can relax to their ground state by multi-phonon emission or light emission at wavelengths different from those characteristic of the lanthanides. These kinds of energy acceptor centers are called killer or quenching traps, and acts as energy sink within the chain transfer, thus quenching the luminescence of the lanthanide ions. The second type of mechanisms is due to energy dissipation via cross relaxation by means of resonant energy transfer between two identical adjacent centers. At large concentrations new kind of centers can be formed, due to clustering of the individual ions. This leads to rearrangements of the energy levels that can strongly affect the fluorescence properties [17].

Fig. 3(A), shows the PL spectra of CaAlBO$_4$:xDy$^{3+}$ phosphors excited by 351 nm light. The PL intensity of both blue and yellow emissions increases with the growing content of Dy$^{3+}$ ions until reaching a maximum at $x=0.50$ mol.% and then it decreases because of concentration quenching, as shown in Fig 3(B).

Obviously, the optimal dopant concentration of Dy$^{3+}$ is 0.5 mol.%, which means the PL intensity of emission peaks decrease while the doped content is above 0.5 mol. % because of the quenching concentration of Dy$^{3+}$. The critical distance $R_c$ of the energy transfer between the same activators Dy$^{3+}$ in CaAlBO$_4$ phosphor could be estimated according to the following equation [18,19].

$$ R_c = \frac{2(V \pi x Z)^{1/3}}{X_c} \approx 2\left(\frac{V 4\pi Z}{X_c}\right)^{1/3} $$

Where $X_c$ is the critical concentration, $Z$ is the number of Ca$^{2+}$ ions in the unit cell and $V$ is the volume of the unit cell. By taking experimental value and analytical values of $X_c$, $Z$ and $V$ (0.005, 6 and 721.705 Å$^3$), the critical transfer distance of Dy$^{3+}$ in CaAlBO$_4$:xDy$^{3+}$ phosphor was estimated to be about 35.81 Å.

3.3 PL characteristics of CaAlBO$_4$:Eu$^{3+}$
concentrations PL intensity is weak. Hence material is from 570 nm to 650 nm which are attributed to the transition increasing concentration of Eu in CaAlBO4, which indicates and selection rule for magnetic dipole (MD) transition is centered at 614 nm is attributed to the electric dipole (ED) transition is.

Two resolved peaks are observed around 592 nm and 614 nm, which are assigned due to 5D0 →7F2 transition in the blue region in the same phosphor. The trivalent europium ion is very useful for studying the nature of metal coordination in various systems, owning to its non-degenerate emitting 5D0 state and for lamp phosphor.

According to equation 1, the critical distance between Eu3+ ions of CaAlBO4:xEu3+ phosphor was estimated to be 48.60Å, by taking experimental value and analytical values of Xc, Z and V (0.002, 6 and 721.705 Å).

4. Conclusions

Rare earth doped CaAlBO4: Dy and CaAlBO4:Eu phosphors by wet chemical method. Blue emission is typical emission of Dy3+ corresponding to 4F9/2 →6H11/2 and yellow emission corresponding to 4F9/2 →6H13/2 transition. The entire characteristic indicates that CaAlBO4: Dy phosphor is good candidate for solid state lighting device application.

The PL emission spectra of CaAlBO4: Eu phosphors suggest that presence of both Eu3+ ion as well as Eu2+ in CaAlBO4 lattice sites. PL revealed that Eu3+ gives broad band emission of orange/red region due to 5D0 →7F2 transition while Eu2+ emission peak due to 4f5d1 →8S2/4f4 transition in the blue region in the same phosphor. The trivalent europium ion is very useful for studying the nature of metal coordination in various systems, owning to its non-degenerate emitting 5D0 state and for lamp phosphor.

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